



## Multiple atmospheric noble gas components in hydrocarbon reservoirs: A study of the Northwest Shelf, Delaware Basin, SE New Mexico

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**Abstract**—The Northwest Shelf of the Delaware Basin, SE New Mexico is the site of several large and productive oil and gas fields. The most productive reservoirs are located in the late Pennsylvanian Morrow and early Permian Abo formations. Production from the latter more important play is predominately from fluvial Abo red beds of the Pecos Slope Field. The oxidizing conditions implied by the reddish color of the formation require an external hydrocarbon source. To test the existing migration model for the region and constrain the location of potential hydrocarbon sources, we measured the elemental and isotopic composition of noble gases produced along with the hydrocarbons. We found the hydrocarbons to be highly enriched in radiogenic  $^4\text{He}$ ,  $^{40}\text{Ar}$  and nucleogenic  $^{21}\text{Ne}$  [ $F(^4\text{He}) = 44,000\text{--}250,000$ ;  $^{40}\text{Ar}/^{36}\text{Ar} = 400\text{--}3145$ ;  $^{21}\text{Ne}/^{22}\text{Ne} = 0.044\text{--}0.071$ ]. The greatest enrichments occur in the Pecos Slope gas fields. The hydrocarbons also contain three independent nonradiogenic noble gas components each with an atmospheric isotopic composition. One component is most likely air-saturated water (ASW). The second component is enriched in the heavy noble gases [ $F(^{130}\text{Xe}) > 8.5$ ] and is derived from the hydrocarbon sources. The third component is enriched in Ne [ $F(^{20}\text{Ne}) > 0.8$ ] that we believe is degassed from sources within the reservoirs. This component is correlated with but decoupled from the dominant source of radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$ . Very high concentrations of  $^4\text{He}$  (up to  $\sim 1\%$  by volume) in the Pecos slope reservoirs require a source external to the reservoirs, such as the underlying Precambrian basement granites and sedimentary equivalents. Structural buckles cutting through the Pecos field may act as high flux vertical pathways for the radiogenic  $^4\text{He}$ . If the hydrocarbons in the Pecos slope fields have migrated northward from the deeper Delaware Basin, as suggested by compositional trends, then perhaps the buckles also play an important role in the distribution and filling of the Pecos slope reservoirs. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

Noble gases associated with subsurface fluids have a wide variety of sources. These sources are identified through their unique isotopic compositions and relative abundance patterns (Hiyagon and Kennedy, 1992; O'Nions and Ballentine, 1993; Ballentine and O'Nions, 1994; Pinti and Marty, 1995; Torgersen and Kennedy, 1999). In hydrocarbon systems, the primary sources are (1) radiogenic noble gases ( $^4\text{He}$ ,  $^{40}\text{Ar}$ ,  $^{21}\text{Ne}$ ,  $^{131\text{--}136}\text{Xe}$ ) produced either in the deep crust or locally in the reservoir or source rock; (2) nonradiogenic noble gases presumably originating from the atmosphere; and (3) to a lesser extent mantle noble gases (Poreda et al., 1986; Hiyagon and Kennedy, 1992; Ballentine et al., 2001), but typically the radiogenic and atmospheric components dominate.

Atmospheric noble gases are identified primarily by the composition of those isotopes for which the radiogenic contribution is negligible and by relative gas abundances (e.g., Ne/Kr/Xe/Ar) determined from the abundance of a nonradiogenic isotope of each noble gas, typically  $^{20,22}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$ , and  $^{130}\text{Xe}$ . In subsurface fluids, the conventional source for the atmospheric noble gases is air-saturated sea, meteoric or connate water (Zartman et al., 1961; Bosch and Mazar, 1988). Water in equilibrium with air will contain dissolved noble gases according to temperature- and salinity-dependent solu-

bility. Noble gases derived from air-saturated water (ASW), therefore, are readily distinguished by atmospheric isotopic compositions and relative abundance patterns which mimic solubility. Evidence for noble gases from ASW in hydrocarbon systems is extensive (see references above) and provides strong support for water acting as an important component in hydrocarbon systems.

Recent evidence has suggested that the hydrocarbon source rocks are also a source of atmospheric derived noble gases (Hiyagon and Kennedy, 1992; Torgersen and Kennedy, 1999). This component has an isotopic composition indistinguishable from air but a relative gas abundance pattern that is highly enriched in the heavy noble gases (Kr and Xe).  $^{130}\text{Xe}/^{36}\text{Ar}$  enrichment factors up to  $\sim 600$  relative to air or  $\sim 200$  relative to water in equilibrium with air have been observed, and it has been shown that this component cannot be derived from ASW by distillation or reequilibration with oil, gas, or oil-gas systems (Torgersen and Kennedy, 1999). Although it is believed that this component was derived originally from the atmosphere, probably from air-saturated sea or ground water, it is treated as a separate component having been isolated from the groundwater system (presumably by absorption favoring the heavy noble gases) and subsequently trapped in the petroleum source rock. As the source rock passes through the oil/gas window, the heavy noble gas-enriched component is expelled and mixed with the hydrocarbon phases (Torgersen and Kennedy, 1999). Support for this hypothesis is provided by laboratory studies indicating that (1) large Kr and Xe excesses

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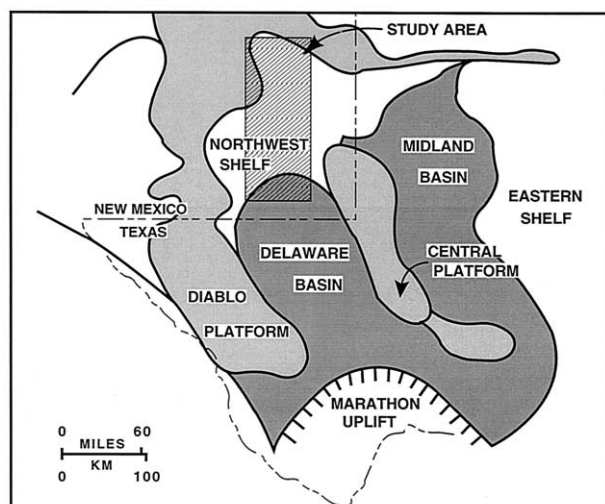


Fig. 1. Simplified map of the Delaware Basin, Northwest Shelf, and surrounding region. Platform areas are lightly stippled, basinal areas densely stippled, and the Northwest Shelf is unshaded. The box with cross-hatching shows the study area.

(relative to  $^{36}\text{Ar}$ ) in carbon-rich and petroleum source rocks are the rule rather than the exception; (2) carbon is the carrier phase for the excess Kr and Xe; and (3) significant quantities of Xe can be carbon-rich materials even at room temperature adsorption (Fanale and Cannon, 1971; Frick and Chang, 1977; Podosek et al. 1980; Podosek et al., 1981). Light (Ne) and heavy (Kr and Xe) noble gas enrichments have also been reported in secondary silica phases, volcanic glasses, tektites, midocean ridge basalts (MORB), and ocean island basalts (OIB) (Barker and Torkelson, 1975; Matsuda et al., 1989; Matsubara and Matsuda, 1995; Matsubara et al., 1988; Pinti et al., 1999). However, the enrichment factors so far observed, at least for Kr and Xe, are significantly smaller than those characteristic of carbon-rich sediments.

In this paper, we present evidence from a study of natural gas fields in southeast New Mexico for a third air-like noble gas component. It is identified by an unusual Ne/Kr/Xe/Ar relative abundance pattern that is unlike ASW or the heavy noble gas-enriched component associated with carbon-rich sediments. Nor is the abundance pattern consistent with distillation of oil-water-gas systems. The noble gas systematics confirm the existing hydrocarbon migration model and provide new insights into noble gas and hydrocarbon sources in the region and the possible role of local structural features on reservoir filling.

## 2. GEOLOGIC SETTING

The northern periphery of the Delaware Basin, SE New Mexico is defined by the Northwest Shelf which extends from the basin north-northwest into central New Mexico (Fig. 1). The Basin sediments gradually thin along the flanks of the Late Paleozoic Pedernal Uplift. Aside from the Pedernal Uplift, there are no major structural features influencing the Northwest Shelf. Minor structures consist of relatively small compaction folds and buckles, which are exposed on the surface in post-Paleozoic rocks. They are parallel linear features trending

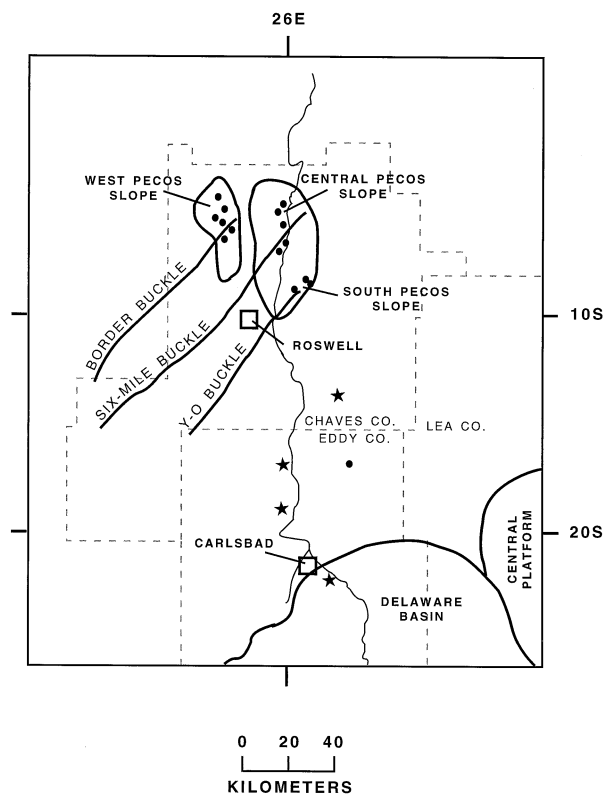


Fig. 2. Enlarged map of the study area showing sampling locations (Abo: solid circles, Morrow: stars) with respect to the Delaware Basin and local structural features.

northeast that can be traced for hundreds of kilometers. It has been suggested that the buckles originated as large shear zones in the underlying Precambrian and continue upward into overlying rocks (Kelley, 1971). The three major buckle structures are shown in the expanded view of the study area (Fig. 2).

The Northwest Shelf area has abundant oil and gas occurrences. Among them is the large and productive Pecos Slope gas field, the main object of this study. The sedimentary formations of the Shelf consist of gently sloping late Pennsylvanian and Permian reefs and banks which prograde into the Delaware Basin (Hills, 1984). Economically important reservoirs are found in the Early Pennsylvanian (Morrow) and Early Permian (Abo) Formations. Both are deltaic-fluvial sequences of sandstones, shales, mudstones, and carbonates. The stratigraphic traps are irregularly shaped sequences of channel and beach sands formed by variations in depositional patterns, cementation, and relative proportions of mudstone (Broadhead, 1984; James, 1985).

Within the Pecos Slope Field, the productive Abo Formation consists of red beds of sand- and mudstones. The reddish color is from ferric iron precipitated with secondary cements in an oxidizing environment during diagenesis, where indigenous organic material would have been consumed by aerobic decay (Broadhead, 1984). South of the Pecos Field, the Permian Abo Formation consists of marine limestones and mudstones that are lithostratigraphically correlated with Abo reef complexes and the Bone Spring Limestone which extend southward into the Delaware Basin (LeMay, 1961; and see also Broadhead,

Table 1. Northwest Shelf, New Mexico oil and gas wells sampled for noble gas analysis.

Sample	Reservoir	Depth (m)	Location	Operator	Well name
Southeast New Mexico					
NM87-01	Abo		25-T17S-R28E	Yates	No. 1 ARCO "EG" State
West Pecos Slope					
NM87-02	Abo	849.2	28-T7S-R23E	Yates	No. 1 Bajillo Draw "WQ"
NM87-57	Abo	929.0	8-T6S-R23E	Memorial	No. 1 "Middle Fork" Federal
NM87-59	Abo	890.2	18-T7S-R23E	Mesa	No. 5 China Federal
NM87-60	Abo	862.9	12-T8S-R22E	Mesa	No. 1 Barn Federal
NM87-62	Abo	893.4	1-T7S-R22E	Mesa	No. 7 Carrot Federal
NM87-63	Abo	898.6	32-T6S-R23E	Memorial	No. 1 Macho State
Central Pecos Slope					
NM87-04	Abo	1188.9	32-T5S-R25E	Yates	No. 1 Dee "OQ" State
NM87-08	Abo	1164.6	14-T7S-R25E	Yates	No. 5 Thorpe "MI" Federal
NM87-09	Abo	1112.2	9-T8S-R25E	Yates	No. 5 Williamson "LC" Federal
NM87-64	Abo	1182.6	3-T8S-R25E	Yates	No. 3 Duncan Federal
South Pecos Slope					
NM87-07	Abo	1439.1	15-T9S-R26E	Yates	No. 2 Spear "OA"
NM87-56	Abo-Perm	1585.9	34-T8S-R27E	Schellinger	No. 1 Campbell Station Unit
NM87-61	Abo-Penn	1944.8	34-T8S-R27E	Schellinger	No. 1 Campbell Station Unit
Morrow					
NM87-03	Mix		24-T17S-R25E	Yates	No. 1 City of Artesia "EQ"
NM87-03	Morrow	2418.4	23-T14S-R27E	Yates	No. 1 Long Arroyo "OW"
NM87-03	Morrow	2739.5	2-T19S-R25E	Yates	No. 1 Rio Penasco "KD" Com.
NM87-03	Morrow	3500.9	19-T22S-R27E	Cities Service	No. 1 Merland "A"

1984). The marine nonoxidized equivalents are considered a potential source facies for the red bed hydrocarbons.

Drilling data (Kelley, 1971) indicate a lack of pre-Permian sequences northwest of the Six-Mile Buckle (Fig. 2). Southeast of this buckle the Pennsylvanian Morrow and older Paleozoic formations occur as a southeast thickening wedge beneath the Permian. Northwest of the Six-Mile Buckle only lower Permian beds, consisting of arkosic sands and granite "wash" eroded from the Pedernal Highlands, separate the Abo from the underlying Precambrian core of the Pedernal Uplift. Despite a close spatial relationship between the buckles and the reservoirs of the large and productive Pecos Slope gas field on the Northwest Shelf, it has been argued that the buckles do not control the occurrence, distribution, or production of natural gas (Broadhead, 1984).

The local oxidized lithologies of the Pecos Slope field do not provide suitable hydrocarbon source rocks, requiring an external source for the hydrocarbons. Broadhead (1984) suggested a source in the nonoxidized marine equivalents of the Abo (and Morrow) formations located to the south within the deeper Delaware Basin. His arguments are based on similarities in the composition of the hydrocarbons in Abo and Morrow reservoirs and the structural and stratigraphic situation of the Northwest Shelf in which the pattern of paleodrainage channels now would facilitate northward migration of hydrocarbons.

### 3. SAMPLES AND EXPERIMENTAL PROCEDURES

A list of the sampled wells is given in Table 1, and their locations are shown in Figure 2. Except for sample NM87-01, all the Abo samples are from wells producing gas from the Permian red beds of the Pecos Slope Field, Chaves County. These samples are subdivided into three groups by location: West, Central, and South Pecos Slope. Abo sample NM87-01 is from a well producing natural gas from the Abo reef complex,

the marine equivalent of the Pecos Slope reservoirs (Broadhead, 1984) located south of the Pecos Slope fields, in the vicinity of the Morrow samples. The tabulated depths are mean perforation depths (meters). Sample NM87-03 is a co-mingled gas representing three reservoirs: lower Permian Wolfcampian (2001 m), upper Pennsylvanian Cisco (2480 m), and Morrow (2601 m). Surprisingly the noble gas composition of the co-mingled gas is indistinguishable from the other Morrow wells. This suggests that either the Cisco and Wolfcampian gases are identical to the Morrow or the Morrow reservoir dominates the noble gas inventory. Sample NM87-58 was collected as a representative sample of the Morrow reservoir in the deeper Delaware Basin located further to the south.

Field operators collected gas samples from the vapor side of well head gas-liquid separators in preevacuated 1000-cc stainless steel cylinders sealed at each end with high-pressure valves. The high gas/(oil + water) ratios reported by the field operators suggests that the noble gases are nearly completely partitioned (>95%) into the gas phase. Therefore, we assume that the separator gas represents the sum of the downhole (reservoir) noble gas concentrations (Ballentine et al., 1996). Small ~15–30 ccNTP aliquots were taken from each cylinder for noble gas analysis which was performed in the RARGA laboratory, University of California and Lawrence Berkeley National Laboratory, Berkeley, CA. The Rouins Automated Rare Gas Analysis (RARGA) laboratory consists of an all-metal gas purification line designed specifically for reactive gas clean-up of "dirty" fluid samples, and is connected directly to an all-metal noble gas mass spectrometer. Analytical procedures can be found in Smith and Kennedy (1983) and Kennedy et al. (1985). A detailed description of the purification procedures employed for the hydrocarbon-rich samples can be found in Hiyagon and Kennedy (1992).

Table 2. Noble gas concentrations and relative abundances, Northwest Shelf, New Mexico.

Sample	Reservoir	Depth (m)	$^{36}\text{Ar}/\text{CH}_4 \times 10^{-7}$ cc/cc	F( $^4\text{He}$ )	+/-	F( $^{20}\text{Ne}$ )	+/-	F( $^{84}\text{Kr}$ )	+/-	F( $^{130}\text{Xe}$ )	+/-
Southeast New Mexico											
NM87-01	Abo		0.129	59640.0	3303.0	0.346	0.035	2.705	0.037	10.72	0.65
West Pecos Slope											
NM87-02	Abo	849.2	2.060	251936.0	20562.0	0.769	0.922	1.696	0.029	4.57	0.43
NM87-57	Abo	929.0	1.610	184560.1	2972.9	0.826	0.027	1.654	0.015	4.52	0.19
NM87-59	Abo	890.2	1.616	202334.9	3064.6	0.645	0.028	1.702	0.013	4.73	0.19
NM87-60	Abo	862.9	1.493	247219.3	4404.1	0.796	0.031	1.656	0.013	4.24	0.14
NM87-62	Abo	893.4	2.439	153411.7	2313.3	0.714	0.014	1.733	0.010	5.09	0.20
NM87-63	Abo	898.6	1.640	219774.8	3452.8	0.794	0.024	1.617	0.012	4.27	0.19
Central Pecos Slope											
NM87-04	Abo	1188.9	2.048	162729.0	12408.0	0.601	0.858	1.709	0.038	4.06	0.29
NM87-08	Abo	1164.6	1.417	209573.0	11640.0	0.533	0.212	1.692	0.025	4.25	0.28
NM87-09	Abo	1112.2	0.176	44302.0	2506.0	0.301	0.283	2.682	0.039	10.92	0.66
NM87-64	Abo	1182.6	1.975	175155.6	3672.3	0.534	0.025	1.668	0.013	4.04	0.18
South Pecos Slope											
NM87-07	Abo	1439.1	1.086	174741.0	9834.0	0.435	0.123	1.718	0.024	4.02	0.26
NM87-56	Abo-Perm	1585.9	0.798	112845.5	2690.0	0.450	0.019	1.978	0.023	5.58	0.26
NM87-61	Abo-Penn	1944.8	1.067	105336.5	1469.5	0.399	0.020	2.024	0.015	5.80	0.33
Morrow											
NM87-03	Mix		0.310	71503.0	3950.0	0.202	0.631	2.583	0.036	9.60	0.63
NM87-05	Morrow	2418.4	0.286	68027.0	3852.0	0.251	0.122	2.513	0.034	8.85	0.54
NM87-06	Morrow	2739.5	0.234	78497.0	4331.0	0.323	0.180	2.529	0.035	9.75	0.59
NM87-58	Morrow	3500.9	0.221	60819.3	861.0	0.465	0.011	2.585	0.021	10.76	0.36
10°C ASW			13.37	0.22		0.272		1.941		3.68	
80°C ASW			6.16	0.52		0.496		1.523		2.27	
Air values used in normalization			316.07	0.167		0.524		0.0207		0.000113	

#### 4. RESULTS

The results are summarized in Table 2 (noble gas elemental compositions and concentrations), Table 3 (helium, neon, and argon isotopic compositions), and Table 4 (calculated ratios of nucleogenic and radiogenic noble gas pairs). In all cases, one

sigma uncertainties are tabulated. The elemental compositions are given as F(i) values which are fractionation factors relative to atmospheric composition using  $^{36}\text{Ar}$  as the reference, e.g.,  $F(^4\text{He}) = (^4\text{He}/^{36}\text{Ar})_{\text{sample}} / (^4\text{He}/^{36}\text{Ar})_{\text{air}}$ . As reported by the producers,  $\text{CH}_4$  is the dominant species with concentrations greater than ~90% by volume. Therefore the  $^{36}\text{Ar}$  concentra-

Table 3. Helium, neon, argon isotopic compositions, Northwest Shelf, New Mexico.

Sample	Reservoir	Depth (m)	R/Ra	+/-	$^{20}\text{Ne}/^{22}\text{Ne}$	+/-	$^{21}\text{Ne}/^{22}\text{Ne}$	+/-	$^{38}\text{Ar}/^{36}\text{Ar}$	+/-	$^{40}\text{Ar}/^{36}\text{Ar}$	+/-
Southeast New Mexico												
NM87-01	Abo		0.0465	0.0087	9.533	0.279	0.04616	0.00080	0.1870	0.0016	482.3	3.9
West Pecos Slope												
NM87-02	Abo	849.2	0.0989	0.0049	9.186	0.129	0.06030	0.00059	0.1834	0.0016	3145.3	36.2
NM87-57	Abo	929.0	0.0268	0.0035	9.528	0.077	0.05390	0.00058	0.1810	0.0054	2750.9	51.6
NM87-59	Abo	890.2	0.0589	0.0129	8.288	0.578	0.05708	0.00058	0.1798	0.0057	2838.6	51.4
NM87-60	Abo	862.9	0.0922	0.0115	9.458	0.075	0.90042	0.00060	0.1807	0.0064	2853.8	58.2
NM87-62	Abo	893.4	0.0383	0.0055	9.761	0.090	0.05368	0.00057	0.1830	0.0038	2564.9	46.3
NM87-63	Abo	898.6	0.0907	0.0050	9.666	0.077	0.05714	0.00056	0.1791	0.0064	2900.1	53.9
Central Pecos Slope												
NM87-04	Abo	1188.9	0.0527	0.0037	9.002	0.308	0.06722	0.00079	0.1828	0.0022	2618.1	88.9
NM87-08	Abo	1164.6	0.0695	0.0060	9.059	0.096	9.07088	0.00069	0.1848	0.0015	2905.9	23.6
NM87-09	Abo	1112.2	0.0173	0.0082	9.893	0.247	0.04506	0.00102	0.1897	0.0015	408.0	3.5
NM87-64	Abo	1182.6	0.0790	0.0054	9.302	0.073	0.07106	0.00072	0.1799	0.0061	2949.0	68.3
South Pecos Slope												
NM87-07	Abo	1439.1	0.1300	0.0075	9.024	0.095	0.07100	0.00069	0.1815	0.0166	2650.8	21.4
NM87-56	Abo-Perm	1585.9	0.1384	0.0098	9.604	0.209	0.06013	0.00123	0.1861	0.0019	2292.9	58.8
NM87-61	Abo-Perm	1944.8	0.1123	0.0055	9.390	0.078	0.05552	0.00055	0.1856	0.0015	2184.4	37.4
Morrow												
NM87-03	Mix		0.0303	0.0046	9.524	0.122	0.04778	0.00053	0.1918	0.0017	449.0	3.6
NM87-05	Morrow	2418.4	0.0423	0.0028	9.433	0.272	0.05169	0.00074	0.1856	0.0017	435.6	3.5
NM87-06	Morrow	2739.5	0.0319	0.0070	8.292	0.119	0.05242	0.00094	0.1869	0.0016	424.0	3.3
NM87-58	Morrow	3500.9	0.0164	0.0091	9.557	0.098	0.04436	0.00056	0.1874	0.0005	424.2	7.3
Air			1.0000		9.800		0.02900		0.1880		295.5	

Table 4. Calculated ratios of nucleogenic and radiogenic noble gas pairs, Northwest Shelf, New Mexico.

Sample	Reservoir	Depth (m)	$^{21}\text{Ne}/^4\text{He} \times 10^{-7}$ cc/cc	+/-	$^{40}\text{Ar}/^4\text{He}$ cc/cc	+/-
Southeast New Mexico						
NM87-01	Abo		0.343	0.044	0.0188	0.0011
West Pecos Slope						
NM87-02	Abo	849.2	0.345	0.389	0.0677	0.0056
NM87-57	Abo	929.0	0.379	0.016	0.0797	0.0021
NM87-59	Abo	890.2	0.393	0.027	0.0753	0.0019
NM87-60	Abo	862.9	0.346	0.016	0.0620	0.0018
NM87-62	Abo	893.4	0.371	0.013	0.0886	0.0022
NM87-63	Abo	898.6	0.334	0.013	0.0710	0.0018
Central Pecos Slope						
NM87-04	Abo	1188.9	0.522	0.686	0.0855	0.0073
NM87-08	Abo	1164.6	0.388	0.144	0.0746	0.0042
NM87-09	Abo	1112.2	0.340	0.324	0.0152	0.0010
NM87-64	Abo	1182.6	0.448	0.023	0.0907	0.0030
South Pecos Slope						
NM87-07	Abo	1439.1	0.383	0.102	0.0807	0.0046
NM87-56	Abo-Perm	1585.9	0.413	0.027	0.1060	0.0040
NM87-61	Abo-Penn	1944.8	0.351	0.019	0.1074	0.0026
Morrow						
NM87-03	Mix		0.182	0.554	0.0129	0.0008
NM87-05	Morrow	2418.4	0.292	0.138	0.0123	0.0008
NM87-06	Morrow	2739.5	0.434	0.207	0.0098	0.0006
NM87-58	Morrow	3500.9	0.403	0.019	0.0127	0.0007
Average crust			1.000		0.2000	

tions are approximately equivalent to the  $^{36}\text{Ar}/\text{CH}_4$  ratio. In Table 3, the helium isotopic compositions (R/Ra) are the measured  $^3\text{He}/^4\text{He}$  ratios (R) normalized to the ratio in air (Ra,  $1.4 \times 10^{-6}$ ). For comparison, the elemental and isotopic composition of noble gases in water in equilibrium with air at 10 and 80°C (ASW) and the air normalization ratios are also included in the data tables.

From the results in Tables 2, 3, and 4 the following observations can be made:

- (1) The noble gas elemental compositions and concentrations and the helium and argon isotopic composition display systematic variation with reservoir (perforation) depth and geographical location. This is illustrated in Figure 3 where  $^4\text{He}/\text{CH}_4$  is plotted against well perforation depth. Note from Table 1 that the well perforation depths increase from North to South.
- (2) Two samples produced from the Abo formation (NM87-01 and NM87-09) are compositionally indistinguishable from the samples produced from the Morrow formation. These and the Morrow samples are compositionally indistinguishable from the Morrow sample collected from a well within the Delaware Basin (NM87-58; labeled DB in Figs. 3, 7, and 8).
- (3) The natural gases produced from the Abo and Morrow Formations are strongly enriched in radiogenic helium [ $\text{F}(^4\text{He}) = 44,000\text{--}250,000$ ,  $^3\text{He}/^4\text{He} = 0.02\text{--}0.14$  Ra], radiogenic  $^{40}\text{Ar}$  ( $^{40}\text{Ar}/^{36}\text{Ar} = 400\text{--}3145$ ), and nucleogenic  $^{21}\text{Ne}$  ( $^{21}\text{Ne}/^{22}\text{Ne} = 0.044\text{--}0.071$ ). The samples from the Morrow formation (and the two from the Abo formation mentioned above in point 2) have undergone the least enrichment, whereas the samples from the Abo formation have undergone the most enrichment, with the enrichment apparently increasing as one moves north up

slope along the Shelf away from the Delaware Basin (Fig. 3).

- (4) The nonradiogenic noble gases in each subfield reservoir (West Pecos Slope [WPS], Central Pecos Slope [CPS], South Pecos Slope [SPS], Morrow, and the marine equivalent of the Abo south of the Pecos Slope) have a unique composition, and surprisingly none match the composition of air or ASW.
- (5) The samples most strongly enriched in radiogenic noble gases are from reservoirs that are located in close proximity to the buckles (Fig. 2).

## 5. MIGRATION MODEL AND NOBLE GAS COMPONENTS

All the observations made above are consistent with a hydrocarbon migration model as postulated by Broadhead (1984), who hypothesized a southern source in the nonoxidized marine equivalents of the Abo sequence and subsequent northward migration along paleo-drainage channels. However, the similarity in noble gas composition between the Morrow, the marine equivalents of the Abo and the Delaware Basin samples suggests the source region may be further south in the deeper Delaware Basin.

This suggests that hydrocarbons with noble gas characteristics like the Morrow samples interacted during or after reservoir filling with noble gases specific for the Pecos Slope reservoir area. From Figure 4 and Tables 2, 3, and 4 a specific noble gas component structure for both "end-member" situations can be determined.

- (1) Morrow type noble gases have  $\text{F}(^{20}\text{Ne})$  values not unlike 10°C ASW (Fig. 4a, Table 2), are enriched in heavy noble gases [ $\text{F}(^{84}\text{Kr})$  and  $\text{F}(^{130}\text{Xe})$ ] compared to ASW and air

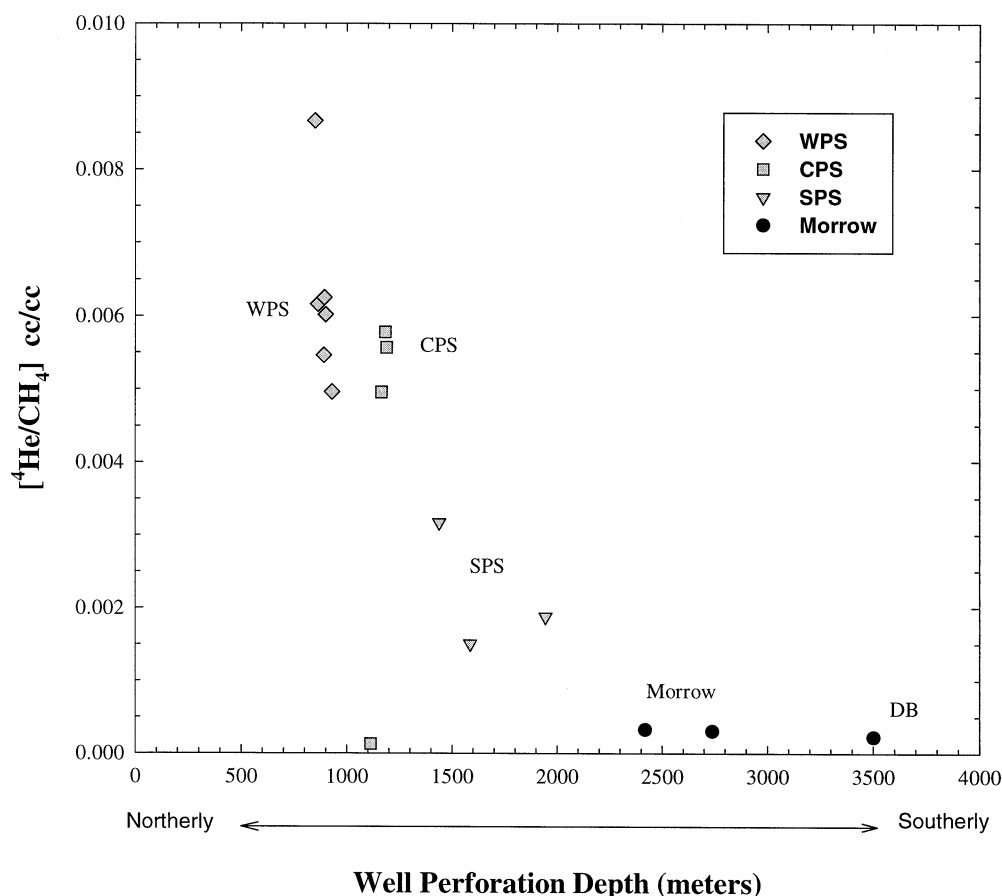


Fig. 3.  $^4\text{He}/\text{CH}_4$  variations as a function of the average well perforation depth. The sample symbols are: Abo, West Pecos Slope (WPS): diamonds; Abo, Central Pecos Slope (CPS): squares; Abo, South Pecos Slope (SPS): inverted triangles; and Morrow: circles. The Morrow sample with a perforation depth of  $\sim 3500$  m is from the Delaware Basin (DB).

(Figs. 4b, 4c, Table 2), and are somewhat enriched in nucleogenic  $^{21}\text{Ne}$  and radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$ , with a fairly constant  $^{40}\text{Ar}/^4\text{He}$  ratio of 0.10 to 0.19 (Tables 3 and 4).

- (2) Pecos Slope type noble gases have  $F(^{20}\text{Ne})$  values significantly greater than  $10^\circ\text{C}$  ASW (eg., Fig. 4a, Table 2), have  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  values not unlike  $10^\circ\text{C}$  ASW (Figs. 4b, 4c, Table 2), and are strongly enriched in nucleogenic  $^{21}\text{Ne}$  and radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  (Table 3).

The possible origin and mechanism of formation of these noble gas components and the possible implications of their presence for the hydrocarbon system are discussed next.

## 6. COMPONENT SOURCES

In this discussion four noble gas components are considered in the following order: (1) the ASW-derived nonradiogenic component; (2) the heavy (Kr, Xe) noble gas-enriched nonradiogenic component; (3) the radiogenic component; and (4) the Ne-enriched nonradiogenic component.

### 6.1. The ASW-derived Nonradiogenic Component

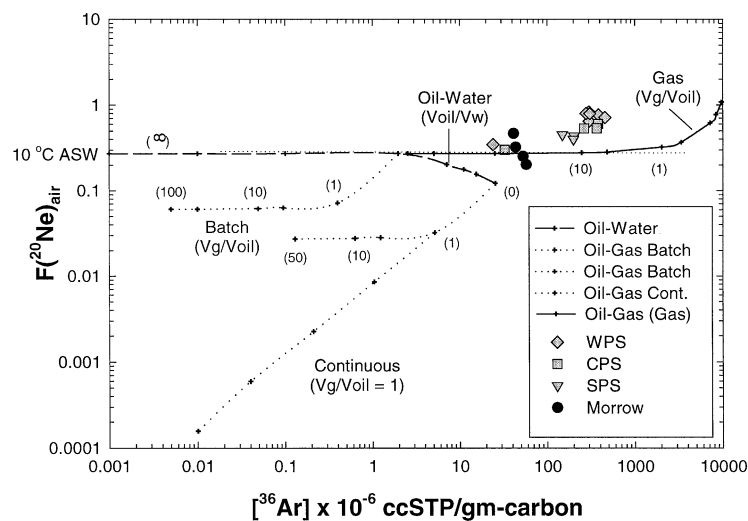
Hydrocarbon samples from both the Morrow and the Pecos Slope show evidence for a noble gas component derived from

$\sim 10^\circ\text{C}$  ASW. In the case of the Morrow hydrocarbons the evidence is  $F(^{20}\text{Ne})$  values that are indistinguishable from  $10^\circ\text{C}$  ASW and for the Pecos Slope samples by  $10^\circ\text{C}$  ASW-like  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  values. In both cases, any other evidence for an ASW-derived noble gas component appears to have been overprinted by noble gas signatures from other sources. For example, it will be shown below that the  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  values for the Pecos Slope hydrocarbons have been overprinted by a  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  signature related to the Ne-enriched nonradiogenic component. The evidence for an ASW-derived noble gas component in this and other studies clearly illustrates the importance of groundwater in establishing the noble gas systematics of hydrocarbon systems. On the other hand, the clear evidence for overprinting of this particular noble gas component suggests that in many cases it is subordinate to the influence of noble gases derived from other sources/components.

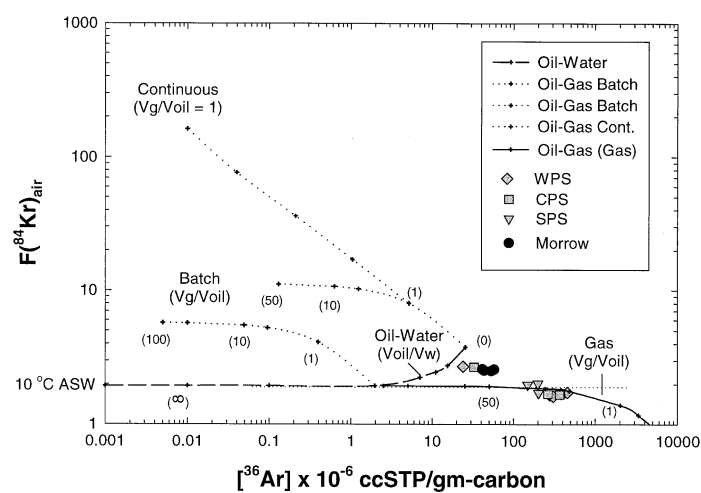
### 6.2. The Heavy (Kr, Xe) Noble Gas-enriched Nonradiogenic Component

As seen in Figures 4b and c, the Pecos Slope gases have  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  compositions similar to ASW, with a slight excess of  $^{130}\text{Xe}$ , whereas the samples from the Morrow

(a)



(b)



(c)

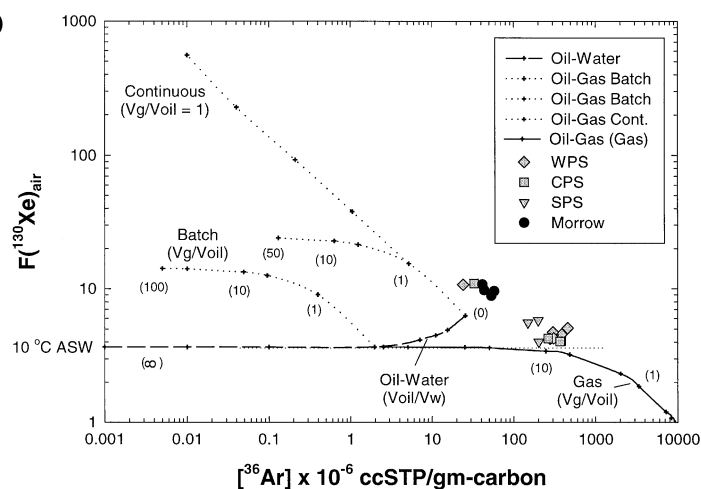


Fig. 4. Noble gas relative abundances normalized to their ratios in air [a:  $F(^{20}\text{Ne})$ ; b:  $F(^{84}\text{Kr})$ ; and c:  $F(^{130}\text{Xe})$ ] and  $^{36}\text{Ar}$  concentrations in the southeast New Mexico gas samples compared to the range of values expected for oil and gas phases according to the oil–water–gas equilibrium solubility model.

reservoirs, the marine equivalents of the Pecos Slope reservoirs, and the Delaware Basin have moderate Kr and large Xe-enrichment factors relative to ASW [ $F(^{84}\text{Kr}) \sim 3$ ;  $F(^{130}\text{Xe}) > 8.5$ ]. Crustal fluids associated with hydrocarbon systems that are enriched in Xe (and Kr) are not uncommon (Bosch and Mazor, 1988; Hiyagon and Kennedy, 1992; Pinti and Marty, 1995; Torgersen and Kennedy, 1999). The isotopic composition requires an atmospheric source. On the assumption that the entire air-derived noble gas budget in hydrocarbon fluids originated in ASW, Bosch and Mazor (1988) presented a model (first proposed by Zartman et al., 1961) in which the noble gas abundance patterns in hydrocarbon fluids were established by equilibrium solubility partitioning between ASW, oil, and gas. Noble gas compositions in the oil and gas phases generated by the solubility equilibrium model are depicted by the dashed, dotted, and solid curves in Figures 4a, b, and c.

For the oil phase, three solubility equilibrium scenarios are considered: oil in equilibrium with water and oil distilled by batch and continuous (Rayleigh) gas loss. Noble gas solubility in oil, particularly heavy noble gases (Kr and Xe), is significantly greater than that in water (Zanker, 1977; Kharaka and Specht, 1988). Therefore, as noble gas-free oil comes in contact with groundwater, the noble gases dissolved in the groundwater will be scavenged by the oil phase, with heavy noble gases scavenged to a greater extent. In Figures 4a, b, and c, the dashed curves represent the noble gas composition of oil in equilibrium with ASW and were constructed assuming ASW last in equilibrium with air at 10°C (10°C ASW) reequilibrated with noble gas-free oil at 80°C. (The noble gas solubility in oil was taken from Zanker, 1977 and is valid for an oil density of 0.85 gm/cm<sup>3</sup>.)

The dotted lines in Figures 4a, b, and c represent the composition of oil previously in equilibrium with water that is distilled either by batch or continuous (Rayleigh) gas loss. Oil–water equilibration and subsequent distillation can generate highly fractionated relative noble gas compositions in the residual oil similar to those observed in oil and gas fields such as the Paris Basin (Pinti and Marty, 1995). However, the large fractionation factors are generated at the expense of gas concentration. It is evident from Figures 4a, b, and c that the samples from the Pecos Slope, the Morrow, and the marine equivalents of the Pecos Slope reservoirs are inconsistent with residual oil compositions, having fractionated noble gas compositions and total concentrations that fall well outside the field defined by the solubility equilibrium model.

The solid lines in Figures 4a, b, and c depict one possible trajectory of gas-phase noble gas compositions in solubility equilibrium with an oil–water system. For illustrative purposes, the initial oil–water composition ( $[^{36}\text{Ar}] = 1.36 \times 10^{-6}$  cc/gm-C;  $F(\text{Ne})$ ,  $F(\text{Kr})$ , and  $F(\text{Xe}) \sim 10^\circ\text{C ASW}$ ) was chosen so that the gas composition trajectory would pass through the Morrow data cluster in Figure 4a. If only the Ne and Ar data are considered, then the composition of the Morrow cluster would be consistent with a gas phase in solubility equilibrium with an oil–water system ( $V_{\text{oil}}/V_{\text{water}} > 100$  cc/cc) at  $\sim 80^\circ\text{C}$  and a  $V_{\text{gas}}/V_{\text{oil}}$  ratio of  $\sim 50$  to 100 cc/cc. However, in Figures 4b and 4c it is clear that the Morrow gases contain significant excesses of Kr and Xe relative to Ne and Ar, such that the Morrow gases cannot be derived from simple solubility equilibrium in an oil–water–gas system. The relative and absolute abundances of

Ne, Ar, Kr, and Xe require an additional source or process. The same is true for the Pecos slope data cluster which is characterized by  $F(^{20}\text{Ne})$  values outside the acceptable range for either gas or oil in solubility equilibrium in a gas–oil–water system. The Pecos Slope Ne excesses will be discussed in more detail below.

Similar inconsistencies in relative abundance patterns with respect to the solubility equilibrium model have been observed in natural gas samples from Alberta, Canada (Hiyagon and Kennedy, 1992), gas fields in the southern San Joaquin Valley, California (Torgersen and Kennedy, 1999), and gas reservoirs in the North Sea (van Soest et al., 2000). These inconsistencies have led to an alternative hypothesis suggesting that excess Xe (and Kr) associated with hydrocarbons represents a component originally trapped in carbon-rich sediments and is, therefore, somehow related to hydrocarbon formation and expulsion (Hiyagon and Kennedy, 1992; Torgersen and Kennedy, 1999). This hypothesis of Xe (and Kr) retention by and subsequent release from carbonaceous sediments has been extensively discussed by Torgersen and Kennedy (1999) for the San Joaquin Valley where  $^{130}\text{Xe}/^{36}\text{Ar}$  enrichments of up to  $\sim 600$  times air were observed. These enrichments and those observed in carbonaceous sediments [ $F(^{130}\text{Xe}) > 4000$ ; Podosek et al., 1980] are much larger than the values observed for the Morrow and equivalent samples in this study [ $F(^{130}\text{Xe})$  8.8–10.9]. However, progressive dilution of such an enriched heavy noble gas component by interaction with ASW-derived noble gases during hydrocarbon expulsion and migration will eventually lead to Xe/Ar and Kr/Ar ratios as observed in the Morrow and equivalent samples. This provides another argument to suggest that the original hydrocarbon source lies further south in the Delaware Basin than initially proposed by Broadhead (1984).

### 6.3. The Radiogenic Component

The very large helium enrichments relative to  $^{36}\text{Ar}$  [ $F(^4\text{He}) > 44,000$  in all samples] combined with low  $^3\text{He}/^4\text{He}$  ratios ( $R/R_a < 0.14$ ) indicates that the helium is dominated by a radiogenic component. In hydrocarbon fluids there are three potential sources for the radiogenic helium: (1) production in the source rock with additional accumulation during migration from source to reservoir; (2) local production within the hydrocarbon reservoirs; or (3) external lithologies, independent of the hydrocarbon source, either from an active or past flux. Spatial trends in the He enrichment factors and discrepancies between measured  $^{40}\text{Ar}/^4\text{He}$  ratios and those predicted by reservoir rock K, U, and Th concentrations can be used to differentiate between these potential sources.

The trend of increasing helium enrichment, as measured by  $F(^4\text{He})$  and  $^4\text{He}/\text{CH}_4$  ratios (Table 2, Fig. 3), with decreasing reservoir depth and increasing distance north from the Delaware Basin is consistent with the pattern that would be expected for  $^4\text{He}$  accumulation in a fluid during progressive migration away from the source (Torgersen and Ivey, 1985). This suggests that production in the source rock with additional accumulation during migration from source to reservoir could be responsible for the radiogenic component.

If the radiogenic gases are produced locally in the carrier strata and if there is little or no He–Ne–Ar fractionation in transit or during release from source minerals, then it would be



Table 5. Concentrations of K, U, and Th, K/(U + Th) ratios, and calculated  $^{40}\text{Ar}/^4\text{He}$  production ratios for core samples, Northwest Shelf and Delaware Basin, New Mexico.

Sample ID	Avg Depth (m)	Formation	Description	K (%)	U (ppm)	Th (ppm)	$[\text{K}/(\text{U} + \text{Th})] \times 10^4$ gm/gm	$(^{40}\text{Ar}/^4\text{He})$
Southeast New Mexico								
YPS-3700	1143	Abo	Red shale	2.41	6.00	11.00	0.142	0.0901
YPS-4300	1326	Abo	Red shale	1.57	5.00	12.00	0.092	0.0644
YRP-8920	2726	Morrow	Gray shale	1.07	3.00	11.00	0.076	0.0614
YRP-9100	2789	Morrow	Gray shale	1.56	6.00	12.00	0.087	0.0568
Average crust							1.100	0.2000

expected that the composition of the accumulated radiogenic component (e.g.,  $^{40}\text{Ar}/^4\text{He}$ ) would match the production rate governed by the K, U, and Th contents of the rocks along the migration path. The K/(U + Th) ratios measured in core samples from the Abo and Morrow reservoirs are relatively constant (Table 5), and the range in the present-day  $^{40}\text{Ar}/^4\text{He}$  production rates calculated from these ratios (Table 5) and normalized to the production rate in average crust (Table 4) are shown as the stippled region in Figure 5. Abo samples from the Pecos Slope (except NM87-09 and -01, located south of the field and representing the marine equivalent of the Pecos Slope reservoirs) plot within this stippled region and their composi-

tions are therefore consistent with production in the Abo and Morrow reservoirs. However, the Morrow, Delaware Basin, and Abo NM87-01 and -09 samples plot well outside the calculated range. This suggests that in these latter reservoirs the accumulated radiogenic components are either fractionated relative to local production or were derived from a source with significantly lower K/(U + Th) ratios. There are three possible fractionation scenarios:

(i) *Mass-dependent diffusive fractionation*: Mass-dependent diffusive fractionation can result from hydrodynamic processes occurring in transit or by differential extraction efficiencies from source minerals. However, by comparing the  $^{40}\text{Ar}/^4\text{He}$

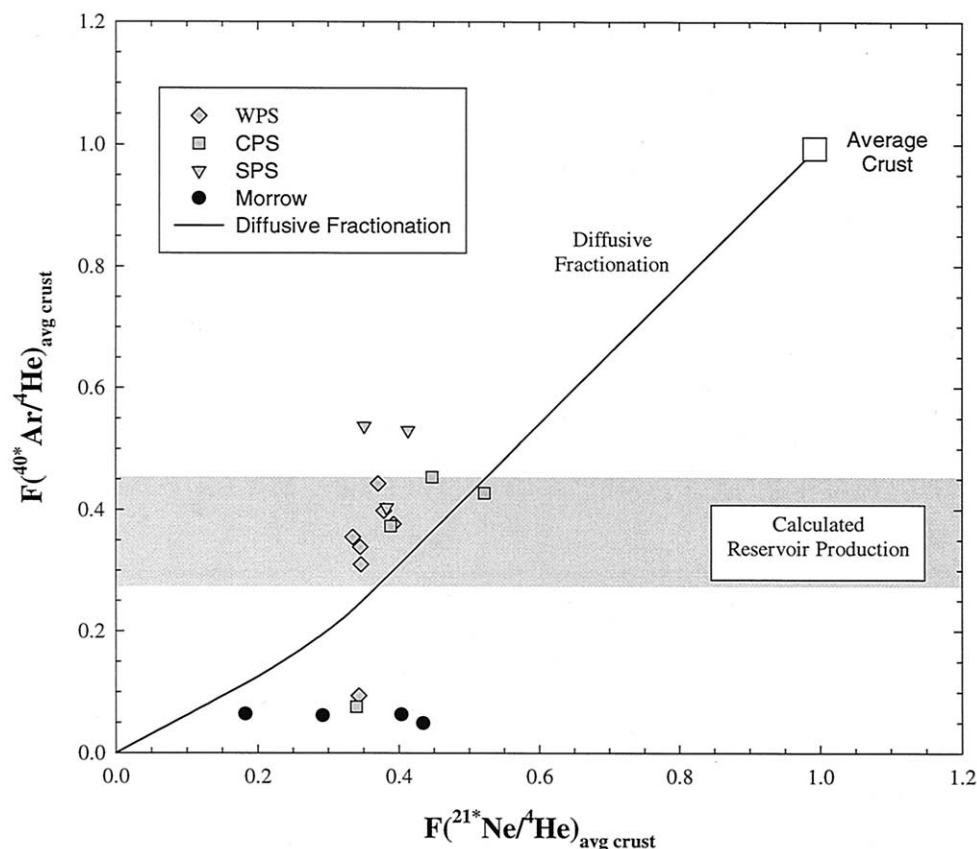


Fig. 5.  $^{40}\text{Ar}/^4\text{He}$  ratios are plotted as a function of the  $^{21}\text{Ne}/^4\text{He}$  ratios. The measured ratios have been normalized to the ratios expected for production in average crust. The data symbols are the same as in Fig. 3. The shaded region represents the expected  $^{40}\text{Ar}/^4\text{He}$  calculated from K, U, and Th contents in core samples from the Abo and Morrow reservoirs and the solid line represents the trajectory for mass-dependent diffusive fractionation.

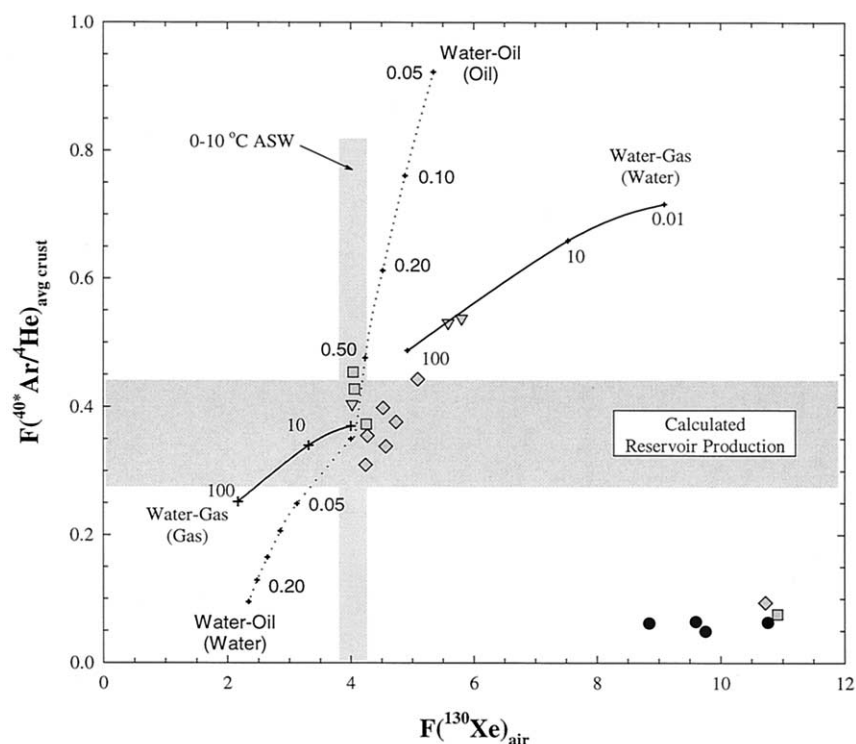


Fig. 6. Measured  $^{40}\text{Ar}/^4\text{He}$  ratios (normalized to the ratio in average crust) plotted as a function of the measured  $^{130}\text{Xe}/^{36}\text{Ar}$  ratios (normalized to the ratio in air). The horizontal shaded region is the same as in Figure 4, as are the data symbols. The vertical shaded region is the range in  $F(^{130}\text{Xe})$  values for 0 to  $10^\circ\text{C}$  water in equilibrium with air (ASW). The curves are distillation trajectories for water–gas and oil–water systems. The numbers along the trajectories are water/gas and oil/water volume ratios.

and  $^{21}\text{Ne}/^4\text{He}$  ratios (Fig. 5), it is readily seen that the compositional differences between the radiogenic components found in the Morrow, Delaware Basin, and Pecos Slope groups can not be the result of mass-dependent diffusive fractionation.

(ii) *Solubility-dependent fractionation:* Compositional changes can also be induced by the different solubility of each noble gas in the oil–water–gas system. Because solubility follows the trend  $\text{He} \sim \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ , the  $^{21}\text{Ne}/^4\text{He}$  ratio is not a sensitive tracer for solubility-driven fractionation. Ideally the  $F(^{40}\text{Ar}/^4\text{He})$  ratios should be compared to the ratio of fissiogenic  $^{136}\text{Xe}/^4\text{He}$ , which has a production ratio that is relatively independent of source chemistry, being determined solely by the U/Th ratio. Unfortunately, for these samples the fission contributions to the xenon isotopic compositions were small or negligible, ranging from 0 to 20‰ for the  $^{136}\text{Xe}/^{130}\text{Xe}$  ratios. In the one case where a sample from the Morrow reservoir can be compared with a Pecos Slope sample, the calculated  $^{136}\text{Xe}/^4\text{He}$  ratios are indistinguishable from each other and that expected for an average crustal U/Th ratio. However, the uncertainties are large and solubility (or diffusive) fractionation can not be conclusively ruled out on the basis of the  $^{136}\text{Xe}/^4\text{He}$  ratios. Therefore, in an attempt to test for solubility fractionation, we are forced to compare the  $F(^{40}\text{Ar}/^4\text{He})$  ratios with a nonradiogenic pair, such as the  $^{130}\text{Xe}/^{36}\text{Ar}$  ratios. Of course, this assumes that the radiogenic and nonradiogenic components are mixed and behave coherently during the fractionation event. In Figure 6, the vertical stippled region signifies  $F(^{130}\text{Xe})$  values for water previously in

equilibrium with air at typical recharge temperatures (0 to  $10^\circ\text{C}$  ASW). Assuming an initial fluid composition at the intersection of the two stippled regions ( $^{40}\text{Ar}/^4\text{He}$ )  $\sim$  local production and  $F(^{130}\text{Xe}) \sim$  0 to  $10^\circ\text{C}$  ASW), the curves depict water–gas (solid) and oil–water (dotted) distillation produced by batch phase separation. The numbers are the water/gas and oil/water volume ratios. It is evident from Figure 6 that the compositional difference between samples from the Pecos Slope and those from the Morrow can not be attributed to distillation unless the high  $F(^{130}\text{Xe})$  ratios in the Morrow samples were acquired after the distillation fractionation of the  $F(^{40}\text{Ar}/^4\text{He})$  values.

(iii) *Preferential or exclusive release fractionation:* Up to this point, it has been assumed that the fractionation process that might be responsible for the compositional differences generates a classic and predictable mass-dependent pattern. The production reservoirs vary in depth from  $\sim 0.8$  to 3.5 km. Assuming a typical geothermal gradient of  $30^\circ/\text{km}$  with an average annual surface temperature, the present-day reservoir temperatures vary from  $\sim 35$  to  $115^\circ\text{C}$ . For some minerals, these relatively low temperatures are below the diffusion closure temperature for Ar and perhaps Ne, but above that for He. Therefore, the low  $F(^{40}\text{Ar}/^4\text{He})$  ratios in the Morrow, Delaware Basin, and NM87-01 and -09 samples (relative to local production) may reflect preferential or exclusive release of radiogenic  $^4\text{He}$  (and  $^{21}\text{Ne}$ ) from host minerals (Ballentine and O’Nions, 1994). However, this seems unlikely because the lowest  $F(^{40}\text{Ar}/^4\text{He})$  ratios, which deviate the most from local

production, are from the deepest (2.5–3.5 km) and therefore hottest reservoirs.

We believe, therefore, that the Morrow gases are derived from a source with a significantly lower  $K/(U + Th)$  ratio than measured in the reservoir rocks. Therefore production in the source rock with additional accumulation during migration from source to reservoir can be excluded as the source of the radiogenic noble gases. However, it does not exclude local production within the reservoir for the Pecos Slope samples.

Although the compositions of the radiogenic noble gases (as defined by the  $^{40}Ar/^{4}He$  ratios) in the West and Central Pecos Slope reservoirs are consistent with local production (Figs. 5 and 6), the concentration of radiogenic  $^4He$  in these reservoirs is extremely high, up to  $\sim 6 \times 10^{-3}$  cc/cc or  $\sim 1\%$  by volume. Assuming (1) reservoir porosities of  $\sim 10\%$  (Broadhead, 1984; Bentz, 1988), (2) rock densities of  $2.5 \text{ gm/cm}^3$ , and (3) 100% of the radiogenic  $^4He$  produced locally in the mineral lattices is lost to the reservoir fluid and retained, the  $^4He$  production rate calculated from the U and Th contents in Table 5 requires a minimum accumulation time of  $\sim 300$  My to attain the observed  $^4He$  concentrations. Although not implausible, this model accumulation time seems unreasonable for upper Permian formations, especially since it requires that 100% of the radiogenic  $^4He$  be retained over the lifetime of the reservoir (Torgersen and Clarke, 1985; Torgersen and Ivey, 1985; Torgersen, 1989; Torgersen and O'Donnell, 1991). Although reservoirs are known to retain the identity of gas sources for long periods of time (Ballentine et al., 2001), quantitative 100% retention of these gases has not been demonstrated. On this basis, production within the reservoir as the single source for the radiogenic noble gases is excluded.

To satisfactorily explain the large concentrations of radiogenic  $^4He$  in the Pecos slope reservoirs, a source in addition to in situ production is required. This source, however, must have a comparable  $K/(U + Th)$  ratio to preserve the measured  $^{40}Ar/^{4}He$  ratios. Two likely candidates are (1) grains of the nonmarine fluvial Abo deposits (eroded from the Precambrian Pederal Highlands) that likely contained significant amounts of radiogenic  $^4He$  that accumulated before erosion and deposition, or (2) a flux of radiogenic gas from the underlying facies (Precambrian Pederal basement rocks and their sedimentary equivalents). At present, we can not distinguish between these two candidates. However, it is noteworthy that the Pennsylvanian sequences pinch out north of the Y-O Buckle (see Fig. 2). Therefore, the Permian sequences of the West and Central Pecos Slope directly overlie the basement rocks and their sedimentary equivalents (lower Permian arkosic sands and granite "wash"). The decrease in radiogenic noble gases south of the Y-O Buckle coupled with this structural relationship suggests that the underlying assemblages are the primary source and that the structural buckles may act as vertical pathways feeding the overlying reservoir traps.

#### 6.4. Ne-enriched Nonradiogenic Component

The Pecos Slope samples have  $F(^{84}Kr)$  and  $F(^{130}Xe)$  values similar to  $10^\circ C$  ASW but are enriched in Ne relative to ASW (Figs. 4a, b, and c). The source or process responsible for the excess Ne [ $F(^{20}Ne) \geq 0.3$ ] is enigmatic. Because the absolute Ne concentrations in these samples are very low, air contami-

nation during sampling or sample processing is a potential source of the excess Ne. However, we feel confident that this is not the case because of the following: (1) Air contamination is inconsistent with sampling and sample processing blanks. (2) The compositions within each subfield of the Pecos Slope (WPS, CPS, SPS) are relatively invariant, requiring that the degree of contamination in each sample from a given subfield is the same. Although this is not implausible, it does seem unreasonable. (3) The degree of apparent air contamination must be correlated with the degree of enrichment in radiogenic noble gases: WPS samples have the highest  $F(^{20}Ne)$  and the greatest radiogenic contribution as measured by the  $F(^4He)$ ,  $^{40}Ar/^{36}Ar$ , and  $^{21}Ne/^{22}Ne$  ratios (e.g., Table 2, Fig. 8).

In the discussion of the solubility model with regard to the heavy noble gas component above, in which only the oil and gas phases were considered, it was shown that the Pecos Slope  $F(^{20}Ne)$  values are outside of the field of acceptable values for oil or gas. An alternative source is the equilibrium solubility composition of the water in the oil–water–gas system. If after contact with ASW the oil and gas phases are removed from the system, then the noble gases remaining in the water phase can be highly fractionated and enriched in Ne (Battani et al., 2000). The expected compositions of this water are depicted by the dotted curved lines in Figures 7a and b, which were constructed using a Rayleigh distillation model identical to that of Battani et al. (2000). The degree of Ne enrichment (and Kr – Xe depletion) is a function of the amount of gas removed from the water by the oil phase, which in turn is a function of the oil/water volume ratio. As evident in Figure 7a, Ne enrichment factors significantly greater than those observed in the Pecos Slope samples can be achieved in the water phase by this process. To account for the Pecos Slope compositions by this model, the straight dotted lines have been constructed to represent hypothetical mixing between a Kr–Xe-enriched noble gas component, like that found in the Morrow reservoirs, and the Ne-enriched (Kr–Xe-depleted) distilled water. From the intersection of these mixing lines with the distilled water composition, the fraction of  $^{36}Ar$  remaining in the distilled water to account for the Ne enrichments can be determined. The Ne–Xe data (Fig. 7a) require a fraction of  $^{36}Ar$  remaining in the distilled water that varies from  $\sim 0.08$  (WPS)– $0.30$  (SPS) which is inconsistent with the fraction of  $^{36}Ar$  determined by the Kr–Xe system ( $\sim 0.65$ – $0.80$ ; Fig. 7b). Although the model proposed by Battani et al. (2000) can produce a Ne-enriched component, in this particular system the model breaks down when the full suite of nonradiogenic noble gases is considered, as evident from the required fractions of  $^{36}Ar$  remaining in the distilled water. Therefore, another process or source is required to explain the Ne enrichments. In addition to the inconsistency with the Battani et al. model, the required mixing with a Morrow-like end-member after distillation is also inconsistent with measured gas concentrations. As seen in Figures 4a, b, and c, the Pecos Slope samples all have  $^{36}Ar$  concentrations greater than the Morrow samples and cannot therefore be generated by mixing of the Morrow and Ne-enriched distilled water end-members.

Diffusive fractionation is another process by which Ne excesses can be generated. However, as is the case for the solubility model, the large variation in  $F(^{20}Ne)$  ( $\sim 0.4$ – $0.8$ ) is not accompanied by commiserate variations in  $F(^{84}Kr)$  and

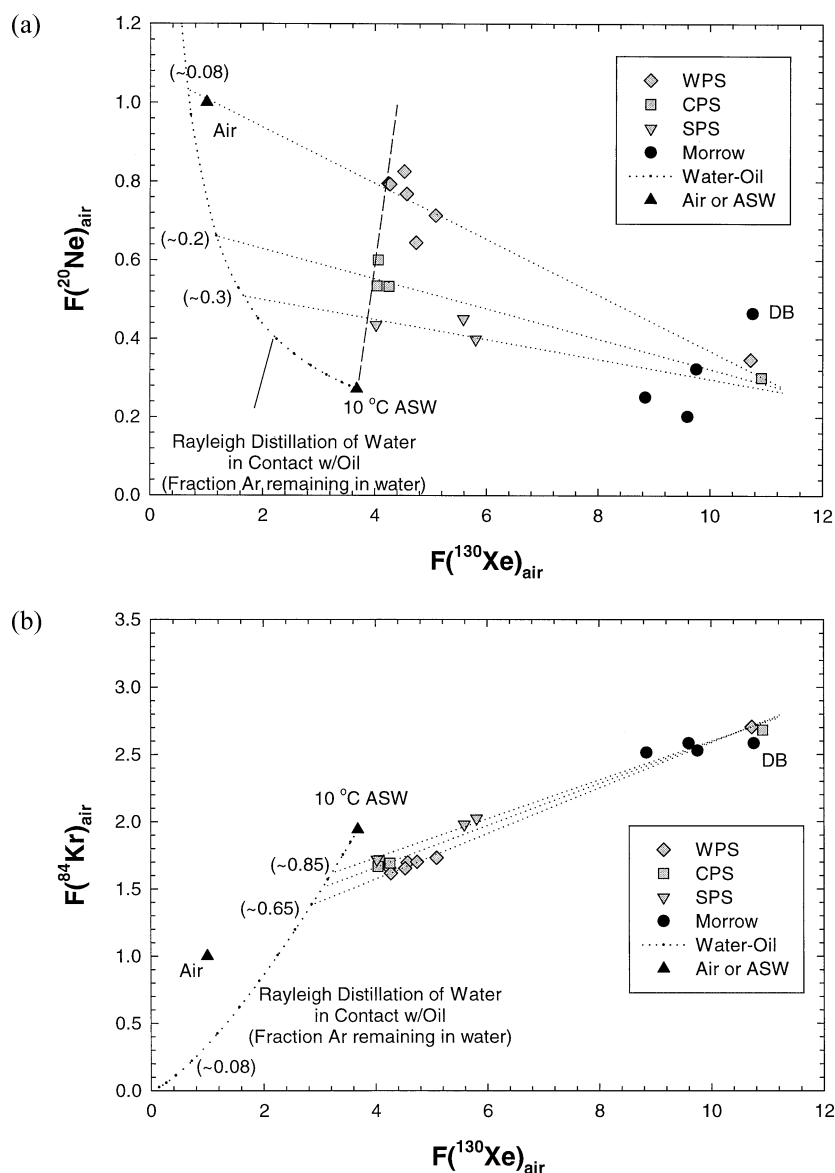


Fig. 7. Noble gas relative abundances [a:  $F(^{20}\text{Ne})$  and b:  $F(^{84}\text{Kr})$ ] vs.  $F(^{130}\text{Xe})$  in the southeast New Mexico gas samples compared to the compositions in air, 10°C ASW and water previously in equilibrium with oil (dotted curve; numbers in parentheses indicate the fraction of  $^{36}\text{Ar}$  remaining in the water). The straight dotted and dashed lines are hypothetical mixing lines.

$F(^{130}\text{Xe})$  as predicted by mass-dependent diffusive fractionation (e.g., Fig. 7a, Table 2).

We suggest that the Ne-enriched air-like component is not related to the oil–water–gas system or generated by mass-dependent diffusive fractionation, but instead may be indigenous to the reservoir, and we suggest two possible sources. (1) Air, in excess of that dissolved in downward percolating water, may become trapped in the recharge water at the boundary between saturated and unsaturated zones through capillary forces (Heaton and Vogel, 1981). Or (2) air-like gases are degassed from sources within the reservoir or from underlying lithologies. The feasibility of each potential source is discussed below.

*Excess air.* Air in excess of that predicted by solubility has

been observed in numerous samples of groundwater (Heaton and Vogel, 1981; Stute and Schlosser, 1993; Ballentine and Hall, 1999; Aeschbach-Hertig et al., 1999, 2000). It is believed that the excesses are caused by trapping or occlusion of air bubbles captured at grain boundaries by capillary forces, followed by total or partial solution at pressures in excess of the ambient atmosphere due to fluctuations in the overlying hydrostatic head. Excesses on the order of 10–20% have been observed. However, excesses approaching 100% by this process, as implied by the West Pecos Slope samples, are unrealistic.

*Degassing of reservoir or underlying lithologies.* As noted above, the fractional and absolute amount of the Ne-enriched air-like component is positively correlated with the absolute

and relative amounts of radiogenic  $^4\text{He}$ , radiogenic  $^{40}\text{Ar}$ , and nucleogenic  $^{21}\text{Ne}$  (Tables 2 and 3). Typically the opposite is observed because the addition of air is expected to dilute the relative amount of these radiogenic components. However, the highest  $F(^4\text{He})$  values (as well as  $^4\text{He}$  concentration and  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios) occur in samples from the West Pecos Slope (Figs. 8a, b, c). This coupling of the radiogenic and nonradiogenic components suggests that the Ne-enriched air-like component is also rock-derived either from devolatilization of the reservoir fluvial deposits or the underlying remnants of the Pedernal Highlands.

The observation of  $F(^{20}\text{Ne})$  excesses should not come as a complete surprise as they are well documented in bulk sedimentary rocks (Podosek et al., 1980; Ozima and Podosek, 1983) and other geologic materials (e.g., secondary silica phases, volcanic ashes, glasses, and OIB and MORB basalts—Barker and Torkelson, 1975; Matsuda et al., 1989; Matsubara and Matsuda, 1995; Matsubara et al., 1988; Pinti et al., 1999). The proportionately large number of cases in which excess Ne was found in sedimentary rocks led Podosek et al. (1980) to conclude that the excess Ne component, originally thought to be exotic, must be considered commonplace.

With this plethora of potential sources for excess  $^{20}\text{Ne}$ , the distinction between an origin in the reservoir rocks themselves or the underlying Precambrian remains an issue. The overall noble gas systematics of the system may provide a clue. The nonradiogenic components of the Pecos Slope reservoirs are a mixture of gases evolved from groundwater previously in equilibrium with air at  $\sim 10^\circ\text{C}$ , a Ne-enriched component derived either locally or from underlying lithologies associated with the Pedernal Uplift, and a Kr- and Xe-enriched component similar to that in the Morrow and marine equivalents of the Pecos Slope reservoirs. A bounding limit for a mixing line between the  $10^\circ\text{C}$  ASW and Ne-enriched components is shown as the heavy dashed line in Fig. 7a. In Figs. 8b and 8c the  $F(^{84}\text{Kr})$  and  $F(^{130}\text{Xe})$  compositions in the Pecos Slope samples remain constant above  $^4\text{He}$  enrichment factors of  $\sim 200,000$ . The same may also be true for  $F(^{20}\text{Ne})$  but the data are not as well constrained (Fig. 8a, Table 2). This invariance leads to an inferred composition for the Ne-enriched component of:  $F(\text{Ne}) \geq 0.8$ ;  $F(\text{Kr}) \sim 1.7$ ; and  $F(\text{Xe}) \sim 4.1$ . The invariance of the  $F(\text{Kr})$  and  $F(\text{Xe})$  values above  $^4\text{He}$  enrichment factors of  $\sim 200,000$ , also suggests that the excess Ne component is decoupled from the radiogenic component with which it is correlated. As discussed above, the radiogenic component apparently has its source in the underlying crystalline basement or its sedimentary equivalents. The decoupling suggests that the excess Ne component does not have its source in that area and therefore may be related to the reservoir rocks. One possibility is that the secondary mineralization of ferric oxide cements, which impart the reddish color to the Abo reservoir rocks (Broadhead, 1984) and indicates an oxygen-rich environment, may have trapped an air-like (Ne-enriched) component. A careful study of core samples from the Abo red beds is needed to evaluate this possibility. If true, a local source for the Ne-enriched component is implied suggesting that the occurrence of this component is decoupled from the hydrocarbons, unlike the Kr- and Xe-enriched component found in the Morrow samples.

## 6.5. The Structural Buckles and Reservoir Filling

As fluid flows north into the Pecos Slope, the processes and sources affecting the Pecos Slope reservoirs will mask the original noble gas composition. These processes include an enhanced flux of radiogenic noble gases from the underlying Precambrian basement and their sedimentary equivalents and acquisition of the Ne-enriched nonradiogenic component. We have argued that the structural buckles, which cross and intersect the Pecos Slope reservoirs (Fig. 2), may act as conduits for the high flux of radiogenic noble gases from lithologies underlying the hydrocarbon reservoirs. However, despite the close spatial relationship between these buckles and the Pecos Slope reservoirs, Broadhead (1984) argued that they have no bearing on the occurrence and distribution of the hydrocarbons. Thus there is an apparent contradiction with respect to the importance of the structural buckles to reservoir filling. If vertical pathways provided by the buckles are also required for hydrocarbon emplacement, then the lack of pre-Permian sequences northwest of the 6-Mile Buckle implies that economic gas reserves will be rare northwest of the Pecos Slope Field. On the other hand, if hydrocarbon emplacement predates buckle formation, then significant gas reservoirs may occur northwest of the Pecos Slope. In this context, it is noteworthy that the buckles extend from the basement into post-Paleozoic sediments where they are exposed on the surface (Kelley, 1971). Unfortunately, the relative timing of hydrocarbon emplacement and buckle formation is not constrained by presently available data.

## 7. SUMMARY

The results of this study into the noble gas systematics of hydrocarbons from the late Pennsylvanian Morrow and early Permian Abo formations of the Northwest Shelf of the Delaware Basin, SE New Mexico are consistent with the existing migration model for hydrocarbons within the region. The model suggests a common source for the hydrocarbons located to the south of the main study area in the nonoxidized marine equivalents of the Abo (and Morrow) formations from which northward migration took place. Compositional trends in the noble gas elemental abundance and isotopic data confirm the migration pattern, but also suggest that the original hydrocarbon source was most likely located further to the south in the Delaware Basin.

The natural gases produced from the Abo and Morrow Formations are (1) strongly enriched in radiogenic  $^4\text{He}$ ,  $^{40}\text{Ar}$ , and nucleogenic  $^{21}\text{Ne}$  and (2) contain mixtures of three independent nonradiogenic noble gas components; each has an atmospheric isotopic composition and each must have a different source.

(i) In samples from both the Abo and Morrow formations, nonradiogenic noble gases derived from ASW form an important component in the total noble gas budget. However, the ASW signature is overprinted by the other components.

(ii) In the Morrow, southern Abo, and Delaware Basin reservoirs, the nonradiogenic noble gas component is enriched in Kr and Xe that was released from the source region along with the hydrocarbons.

(iii) In the Pecos Slope Fields the Xe-enriched component is

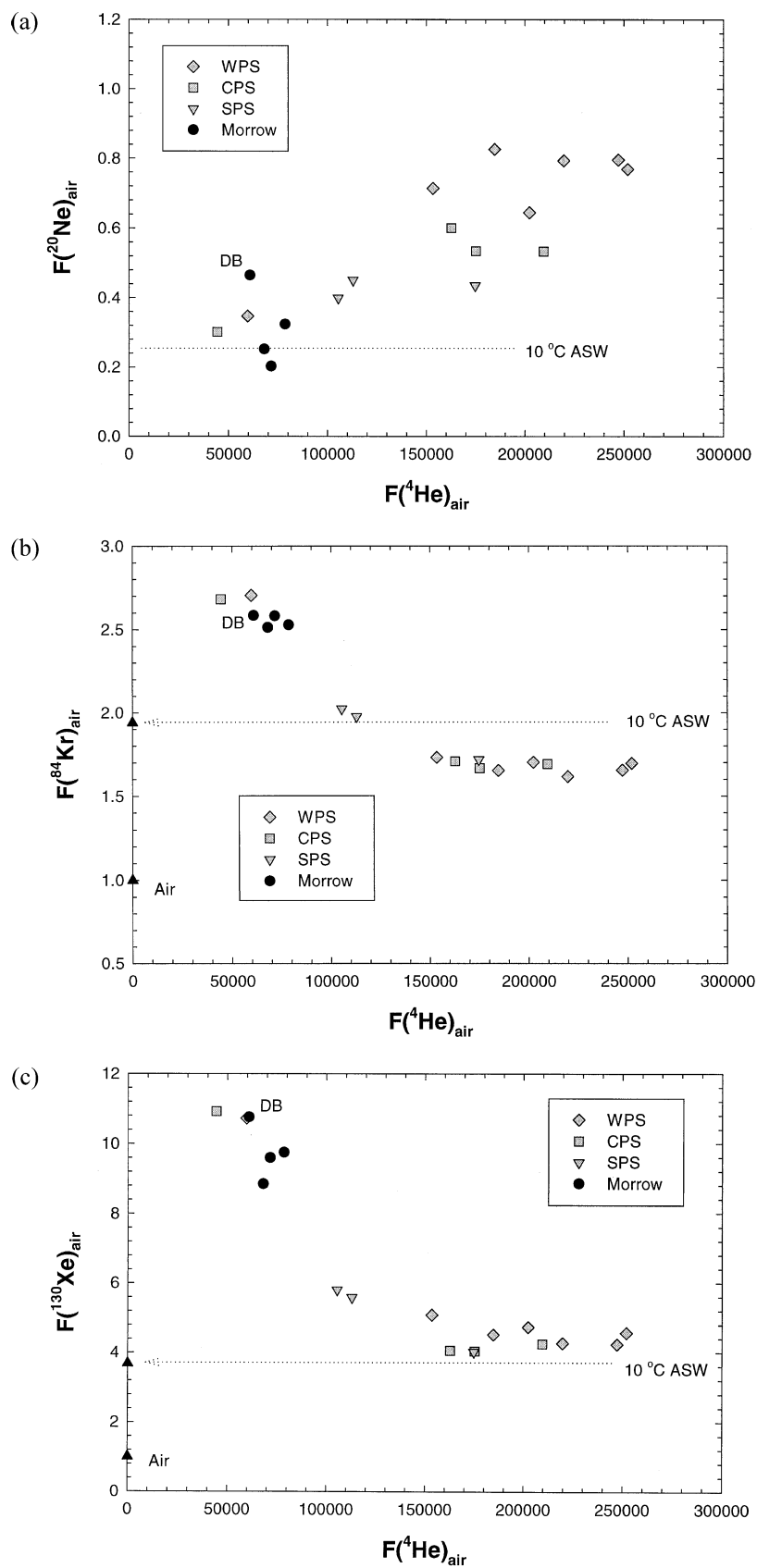


Fig. 8. Relative abundances of the nonradiogenic noble gases plotted as a function of radiogenic helium enrichment factors [a:  $F(^{20}\text{Ne})$ , b:  $F(^{84}\text{Kr})$ , and c:  $F(^{130}\text{Xe})$  vs.  $F(^4\text{He})$ ]. For comparison the compositions of air and 10 °C ASW are also shown.

not as prevalent and the nonradiogenic gases dominating these reservoirs reflect mixing between ASW and a Ne-enriched component.

Surprisingly, the nonradiogenic Ne-enriched component is most evident in the hydrocarbon gases most enriched in radiogenic noble gases. However, although correlated, the radiogenic and Ne-enriched components appear to be decoupled, thus requiring a different source for each. The radiogenic component appears to be derived from the Precambrian basement or equivalent sediments, which underlay the Pecos Slope reservoirs, whereas we believe that the nonradiogenic Ne-enriched component may have been degassed from sources within the reservoir.

High concentrations of radiogenic  $^4\text{He}$  (up to  $\sim 1\%$  by volume) in the Pecos Slope reservoirs require an external source, such as the underlying Precambrian basement and sedimentary equivalents. The structural buckles crossing the Pecos Slope and intersecting the Abo gas reservoirs may provide the necessary vertical flux pathways. If the structural buckles play an important role in hydrocarbon emplacement, then the relative timing of hydrocarbon emplacement and buckle formation may be critical to hydrocarbon distribution. Unfortunately, the present data do not place adequate constraints on this relative timing.

It is evident from this and earlier studies (Torgersen and Kennedy, 1999) that it is no longer safe to assume that air noble gases are introduced to basin fluids exclusively by the direct influence of air-saturated groundwater. In future modeling of basin fluid compositions and flow, it will be necessary to consider the potential presence and influence of at least three independent air noble gas components of different source and implication.

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